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13. ABSTRACT Marine borer resistance of various experimental polymeric materials, otherwise suitable for marine electric cable insulation, was evaluated. Twenty-five candidate formulations containing polyvinyl chloride (PVC) resin were prepared. Four non-PVC formulations containing chlorosulfonated polyethylene, ethylenepropylene rubber, chlorinated polyethylene, and crosslinked polyethylene respectively were also prepared. One commercial plastic, cellulose acetate-butyrate, was included. These plastics were exposed in the Pacific Ocean at Naos Island, C.Z., and in the Caribbean at Coco Solo, C.Z., for periods of 6 months to 14 months. Part of each specimen was exposed directly to the water; the remainder was juxtaposed with Honduran mahogany, partly in the form of a sandwich. No marine boring organisms attacked the plastics directly from the water; all damage occurred at the wood plastic interfaces. None of the formulations were completely immune to attack by both teredos and pholads, although the non-PVC polymers were much more resistant to both than the PVC formulations. The presence of inert fillers or toxicants or a change in plastic hardness in the PVC formulations had little effect on the amount of pholad damage. Tereido damage was not as extreme or extensive as pholad damage. The PVC formulations containing the inert, inorganic fillers were virtually undamaged by teredos; those containing toxicants were also relatively free of damage by these organisms. Creosote as a co-plasticizer protected one of the PVC formulations against teredos. The hardness in PVC plastics was not an important variable. The cellulose acetate-butyrate was heavily damaged by both teredos and pholads.			

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ABSTRACT

Marine borer resistance of various experimental polymeric materials, otherwise suitable for marine electric cable insulation, was evaluated. Twenty-five candidate formulations containing polyvinyl chloride (PVC) resin were prepared. Four non-PVC formulations containing chlorosulfonated polyethylene, ethylenepropylene rubber, chlorinated polyethylene, and crosslinked polyethylene respectively were also prepared. One commercial plastic, cellulose acetate-butyrate, was included. These plastics were exposed in the Pacific Ocean at Naos Island, C.Z., and in the Caribbean at Coco Solo, C.Z., for periods of 6 months to 14 months. Part of each specimen was exposed directly to the water; the remainder was juxtaposed with Honduran mahogany, partly in the form of a sandwich. No marine boring organisms attacked the plastics directly from the water; all damage occurred at the wood plastic interfaces. None of the formulations were completely immune to attack by both teredos and pholads, although the non-PVC polymers were much more resistant to both than the PVC formulations. The presence of inert fillers or toxicants or a change in plastic hardness in the PVC formulations had little effect on the amount of pholad damage. Teredo damage was not as extreme or extensive as pholad damage. The PVC formulations containing the inert, inorganic fillers were virtually undamaged by teredos; those containing toxicants were also relatively free of damage by these organisms. Creosote as a co-plasticizer protected one of the PVC formulations against teredos. The hardness in PVC plastics was not an important variable. The cellulose acetate-butyrate was heavily damaged by both teredos and pholads.

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This is a final report on this project.

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AN INVESTIGATION OF MARINE BORER RESISTANCE OF POLYMERIC MATERIALS

INTRODUCTION

Consonant with man's expanding activities in the sea is the need for reliable information on the performance of a wide variety of engineering materials in the marine environment. While considerable information is available concerning behavior of many natural polymeric materials, e.g., wood, much less is known about the ability of various synthetic polymers to withstand the rigors of the sea. This lack of information becomes critical when expensive marine installations are to be made of which these materials may be a part. One of the most important applications for suitable synthetic organics is that of insulation on marine cables used in communications, electric power transmission, and sensor umbilicals. For this application, a candidate insulating material must possess flexibility, chemical nonreactivity and resistance to damage by marine micro- and macroorganisms.

In a search for synthetic polymers for marine use, Bell Telephone Laboratories (1-6) has engaged in a screening program for several years, exposing a wide variety of proprietary materials in the sea. Similarly, but with a less specific goal, the U.S. Civil Engineering Laboratory (7-10) has engaged in a program of study concerning deep-ocean biodeterioration of proprietary materials. The work described in this report is part of a general program at NRL concerned with marine biodeterioration and its prevention. The experimental approach adopted was to fabricate in the laboratory, under rigorous control, the various plastic formulations to be used for field evaluation and to seek a specific correlation between resistance to attack by macroorganisms and chemical composition which will prove useful in setting specifications. To date 46 different formulations of polyvinyl chloride (PVC) plastic and four formulations of other plastics have been fabricated. All of these formulations are being evaluated as potential insulation materials for use in the terrestrial environment; preliminary data on the behavior of some of these formulations for the above use have already been collected and report (11). In this parallel study 29 of these plastics and one proprietary plastic, cellulose acetate-butyrate, were exposed to the marine environment.

EXPERIMENTAL PROCEDURE

Formulation Variables

The polymer formulations incorporated, variously, three plasticizers, three toxicants, and a wide variety of inert fillers. The composition of each of these experimental plastics is presented in Table 1.

Plasticizers—Commercially available grades of dioctyl phthalate (DOP), dioctyl adipate (DOA), tricresyl phosphate (TCP) fortified with the ortho isomer, and whole creosote were used as plasticizers for the PVC resin. Commercial preparations of TCP, although composed predominantly of the para isomer, contain some of the ortho compound, which exhibits a

Table 1
Composition of Experimental Polymeric Materials

Polyvinyl Chloride (PVC) Formulations*	Form- ula No.	Plasticizer			Plastic Hard- ness	Additives
		DOP	DOA	TCP		
Plastics						
Control	1	100	—	—	53†	None
Increased hardness by decreasing plasticizer	3	—	—	—	22D	None
	4	—	—	—	48D	
	5	—	20‡	—	60D	
	21	0	—	—	80D	
Increased internal hardness, (12) by addition of mineral fillers	6	100	—	—	70	35 Fiberglas, 7% vol
	7	100	—	—	58	54 Silica sand, 270-400 mesh, 10% vol
	8	100	—	—	62	54 Silica sand, 170-270 mesh, 10% vol 1% silane
	9	100	—	—	62	54 Silica sand, 270-400 mesh, 10% vol 1% silane
	10	100	—	—	59	25 Silica sand, 270-400 mesh, 5% vol 1% silane
	11	100	—	—	57	83 Silica sand, 270-400 mesh, 15% vol
	12	100	—	—	60	65 Silicon carbide, 270-400 mesh, 10% vol
	12F	100	—	—	60	65 Silicon carbide, <400 mesh, 10% vol
	25	100	—	—	60	97 Silicon carbide, 400 mesh, 15% vol. 2% silane
	26	100	—	—	80	97 Silicon carbide, 400 mesh, 15% vol
	13	100	—	—	58	53 Dolomite sand, 400 mesh, 10% vol
Toxic additives	I18	100	—	—	63	1.3 Aldrin
	I19	100	—	—	63	2.6 Aldrin
	I20	100	—	—	63	1.3 Dieldrin
	I21	100	—	—	63	2.6 Dieldrin
	I22	100	—	—	63	1.3 Lindane
	I23	100	—	—	63	2.6 Lindane
Plasticizer variation	23	50	—	—	65	50 Creosote (To make 100 parts plasticizer)
	I9	50	—	100	63	—
	I25	—	100	—	63	—
Other Polymer Formulations§						
Chlorosulfonated polyethylene	19	Hypalon (100), Thermax (30), Severin 100(10), litharge (25), MBT (0.5) Tetronea (2)				
Ethylenepropylene rubber	20	Nordel 1070 (100), Philblack A(60), stearic acid (1), process oil (20), Thionex (1.5), MBT (0.5), ZnO (5), sulfur (1.5)				
Chlorinated polyethylene	22	Plaston (100), Epon 828 (6), Philblack A (10), NA-22 (8), sulfur (1)				
Crosslinked polyethylene	24	Petrothene XL 6301 (100)				
Cellulose acetate- butyrate	CA	Obtained commercially				

* All of the PVC formulations are based on 100 parts of resin (B.F. Goodrich-Geon 101) and contain carbon black (2), lead maleate (3.5), dibutyltin laurate (2), and whiting (30), in addition to the tabulated materials.

† All hardness determinations were made with a Shore type A durometer except where indicated by D (Shore type D durometer).

‡ DOA substituted for DOP because the DOP would not blend in these proportions; DOP = dioctyl phthalate, DOA = dioctyl adipate, TCP = tricresyl phosphate.

§ All non-PVC formulations are based on 100 parts of polymer.

general toxicity toward animal organisms. Because of this relationship 30 wt-% of the ortho isomer (o-TCP) was added to the commercial preparation.

Toxicants—Organic materials can be protected from biological degradation by including in their fabrication chemical agents which impart a toxic or repellent quality to the finished product. The toxicants used in this exposure—aldrin, dieldrin and lindane—have had prior trials elsewhere in the formulation of PVC plastics for use in the terrestrial environment. Results of these experiments, however, are inconclusive because of the uncertainty of the degree or retention of the toxicant during the compounding process. In this investigation separate weight-loss studies were made which indicated that under the milling conditions imposed, less than 1% of the added toxicant was volatilized. Because of this closed/control over the addition of these insecticides in compounding the present formulations, the effectiveness of these additives was reexamined, as a means of controlling biological damage not only in the terrestrial environment but also in the marine environment, where leachability of these chemicals when subjected to continuous salt-water immersion must be considered.

Hardness—There are, however, certain disadvantages to the use of such powerful toxicants. These disadvantages are the possible loss in effectiveness over a period of time by leaching, as mentioned above; chemical degradation; the toxicity of the chemicals, which creates personnel handling problems; and the mounting evidence that these polychlorinated organic insecticides are a threat to the ecology of those areas in which they are used, including a direct threat to man via his normal food chain. Because of these factors, the possibility of using hardness-controlling inert fillers as protective agents was investigated. Damage by termites has been shown to have an inverse relationship to hardness for several plastic materials, including PVC (12). This resistance appears to result from mechanical impairment of the termites' mandibular activity. It was considered worthwhile to see whether an impairment of boring activity of marine borers could also be observed. Accordingly, several PVC plastics were formulated in which the hardness was varied. This adjustment was made by a systematic reduction of plasticizer in the formulations or by addition of inert fillers. Hardness achieved by regulation of plasticizer suffers from the disadvantage that it is obtained at the expense of flexibility of the plastic, a necessary property of cable insulation. Alternatively, hardness may be adjusted without serious loss of this characteristic by adding to the formulation finely divided inert material. If it is intrinsically harder than the cutting mechanism of the borers (about 3.5 on the Moh's scale for the aragonite shell of teredo), borer resistance may be improved. Plastic hardness thus achieved is referred to as "internal hardness" (12) and differs from hardness associated with plasticizer reduction. The inert fillers used in this study are included in Table 1.

Compounding

The various plastics were prepared by compounding the ingredients of each formulation on a roller mill operated at 260° to 270° F. The initial mix for each PVC formulation consisted of the resin, whiting, and plasticizer. After these constituents were blended, carbon black, lead maleate, and dibutyltin laurate were added, in the order given. Finally, the appropriate inert filler was added when used. A coupling agent (silane) was also added in some formulations to bind the particles of the inert filler to the plastic so that they could not be mechanically dislodged from the plastic matrix. After thorough mixing of the charge, the rollers were adjusted to give a 50-mil clearance and the plastic sheeted off. When a toxicant was part of the formulation, it was added to the mix just prior to sheeting to allow only minimum exposure to heat. The total milling time for each charge was about 15 to 20 minutes; the milling time for the toxic additives was 5 minutes. The material, as it came from the mill, was sufficiently smooth and uniform to be used directly for preparing the specimens. All sheets were cut into 3-by-5-in. panels for later specimen fabrication. The elastomers were similarly compounded.

Exposure Techniques

The technique devised for exposing the experimental materials in the sea was as follows. Each of the plastic panels was fastened by Monel staples to a piece of 1-by-3-by-5 in. end-grain-cut Honduran mahogany (*Swietenia macrophylla*), which acted as a support for the panel. A second piece of flat-sawn mahogany, 0.5-by-2.5-by-3-in., was used to cover half of the open face of the plastic to form a partial sandwich as shown in Fig. 1; the remaining half of the plastic was left uncovered for direct exposure to seawater. Borer-susceptible wood has been used previously to serve as a coupling agent between the borers and the surface of the plastic (1,9). Mahogany was chosen because of its susceptibility to teredo and pholad attack and its resistance to that of limnoria. Sixteen of these exposure specimens fastened to a 1.5-in. O.D. rigid PVC pipe with nylon nuts and bolts constituted an exposure array as shown in Fig. 1. The first set of specimens, which included all of the inert filler formulations, was exposed in the Bay of Panama. The exposure site, 1.5 miles from the natural shoreline, is located at the Smithsonian biological collection pier adjacent to the Ft. Amador causeway at Naos Island, Canal Zone. The formulations were exposed in quintuplicate and randomly distributed throughout an exposure field composed of twelve specimen arrays. All of the arrays at this site were suspended in the water so as to be 9.5 feet below mean tide; the daily tide at this location is 14 feet and the current about 0.5 knot. The second set of specimens which contained toxicants was placed on exposure in Manzanillo Bay, an arm of the Caribbean, along a sea wall at the deactivated Coco Solo Naval Station, Canal Zone. These formulations were also exposed in quintuplicate and randomly distributed throughout an exposure field composed of four specimen arrays. Very little tide occurs on this side of the Isthmus (1 to 2 feet) and the maximum current is <0.2 knot.

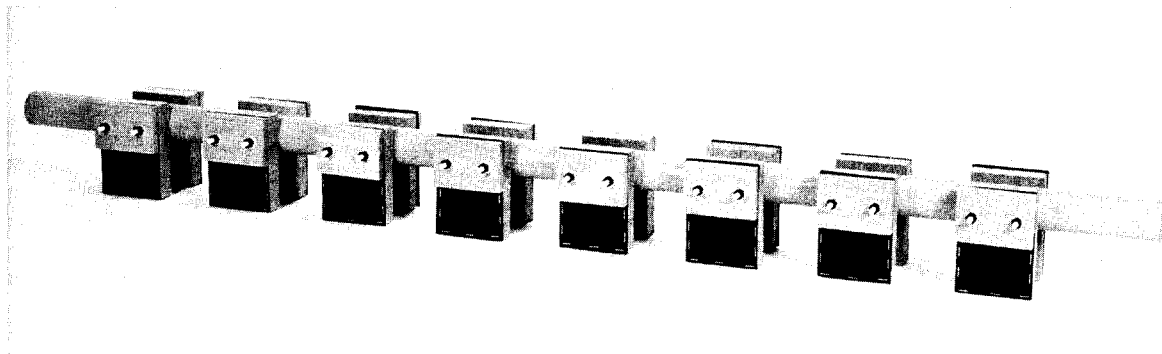


Fig. 1—An exposure array composed of randomly placed specimen units bolted to a 1.5-in. OD rigid PVC pipe; construction details of the individual specimens are apparent

Specimen Rating System

The wood and plastic comprising each exposure specimen were rated separately for borer damage by subjective evaluation. Only those faces of the wood in contact with the plastic were considered, and the rating was based on the total number of borer holes through the surface of the wood, as follows: heavy (3), >30 holes; moderate (2), 10-30 holes; light (1), 1-10 holes, and none (0) when there was no breach in the wood surface. The digitized rating was used to estimate the average damage sustained by each of the three rated surfaces, separately. Each plastic panel was divided into four areas for rating purposes as follows: (a) the surface of the panel in contact with the small, outer mahogany piece of the sandwich, (b) the opposite surface of the panel within the sandwich, (c) the interface between the larger mahogany support piece and the nonsandwiched portion of the panel, and (d) the face of the

panel exposed directly to the water. Each plastic specimen was then rated by counting the penetrations into a given surface as defined above. Frequently, a specimen would be perforated. A separate record of such perforations was kept for each face as it was rated. Those perforations of the specimen originating on the opposite face from that being rated were not counted until the opposite face was rated.

Specimen Removals

Three specimens of each formulation of the first set were removed from the Naos Island exposure site after 8 months in the sea. The remaining specimens were removed from this site after 14 months. Three specimens from the second set were removed from the Coco Solo site after an exposure period of 6 months, and the remaining specimens at this site were removed after 1 year of exposure. The specimens at the time of removal were covered with considerable soft fouling, primarily encrusting bryozoa, and a lesser amount of hard fouling composed of barnacles and tube worms. A similar fouling pattern was encountered on all subsequent removals. Each specimen array was photographed as it was removed from the water (Fig. 2). The array was then disassembled, the individual specimens cleaned of the soft fouling, and the sandwich parted for visual inspection. Specimens were photographed as open sandwiches when particularly large borers (pholads) were found bridging the wood/plastic interface as shown in Fig. 3. The specimens were then soaked in ethyl alcohol for 24 hours to desiccate the animal tissues, dried in an oven at 105°C for an additional 24 hours, and returned to the laboratory for a closer examination.

RESULTS AND DISCUSSION

Results for most of the marine exposures carried out at Naos Island are presented in Table 2; those for the marine exposure carried out at Coco Solo in Table 3. In Table 2 the plastic formulations have been grouped where possible according to a common function as indicated across the top of each grouping. In several instances a formulation contained two variables which made it eligible for placement in more than one group, or it contained a

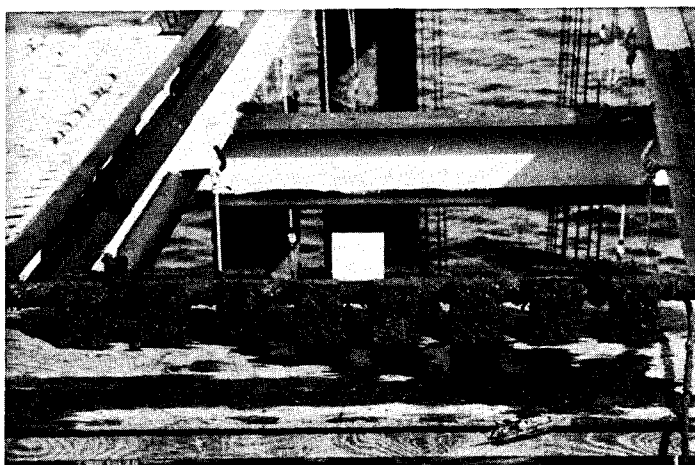


Fig. 2—A specimen array after removal from the water (Naos Island). Both hard and soft fouling organisms are present; the incidence of barnacle settlement was much greater at Coco Solo



Fig. 3—A specimen sandwich opened to show the presence of pholads across the wood/plastic interface

variable which made it difficult to assign to a specific group. The performance of these formulations has been treated separately in Tables 4 and 5.

Table 2
Borer Damage to Polymeric Materials in the Pacific Ocean
(Naos Island, Canal Zone)

Formula No.	Abbreviated Formulations*	8 Months' Exposure			14 Months' Exposure		
		Pholads	Teredos		Pholads	Teredos	
		Surface Penetrations		Etches	Surface Penetrations		Etches
Basic Formulation							
1	Control formulation	22(10) [‡]	7(1)	11	32(22)	32(1)	32
	Intensity of attack [†]	1.67	0.53		3.30	3.30	
Reduced Plasticizer							
3	1/3 Reduction of plasticizer	10(5)	2(0)	13	3(2)	7(0)	20
4	2/3 Reduction of plasticizer	10(6)	4(0)	>31	12(5)	4(0)	3
5	4/5 Reduction of plasticizer	6(4)	7(0)	>10	11(5)	18(0)	24
21	No plasticizer	4(2)	3(0)	2	10(2)	2(0)	—
		30	16		36	31	
	Intensity of attack	1.59	0.85		2.75	2.36	
Inert Fillers							
6	Fiberglas	5(2)	0	—	9(2)	0	—
7	Silicon dioxide, 270-400 mesh—10%	3(1)	0	3	10(5)	0	—
8	Silicon dioxide, 170-270 mesh—10%, 1% silane	5(1)	0	1	—	—	—
9	Silicon dioxide, 270-400 mesh—10%, 1% silane	5(1)	0	4	2(0)	1(0)	3
10	Silicon dioxide, 270-400 mesh—5%, 1% silane	5(2)	0	—	9(7)	0	—
11	Silicon dioxide, 270-400 mesh—15%, 2% silane	2(0)	0	4	7(0)	0	2
12	Silicon carbide, 270-400 mesh—10%	5(2)	0	6	4(2)	0	—
25	Silicon carbide, 270-400 mesh—15%, 2% silane	5(3)	0	—	7(1)	0	5
12F	Silicon carbide, <400 mesh—10%	7(2)	0	—	10(5)	0	—
13	Dolomite, 270-400 mesh—10%	8(0)	0	—	9(2)	0	—
		50	0		67	1	
	Intensity of attack	1.20	0		2.30	0.03	
Other NRL-Formulated Polymers							
19	Chlorosulfonated polyethylene	1(0)	0	6	0	2(0)	12
20	Ethylenepropylene rubber	5(0)	0	4	1(0)	0	20
22	Chlorinated polyethylene	7(0)	0	4	9(0)	2(0)	8
24	Crosslinked polyethylene	3(1)	0	1	9(2)	6(0)	4
		16	0		19	10	
	Intensity of attack	0.85	0		1.40	0.74	
Proprietary							
CA	Cellulose acetate-butyrate	11(10)	21(1)	1	12(10)	19(3)	—
	Intensity of attack	2.39	4.56		3.53	5.58	

* For complete formulations consult Table 1.

† Intensity of attack = penetrations of plastic surface/dm².

‡ The parenthesized figure is the number of perforations of the plastic.

Table 3
Effect of the Addition of Toxicants to the Basic Polyvinyl Chloride Formulation (Coco Solo)

Abbreviated Formulation*	Form- ula No.	6 Months' Exposure				12 Months' Exposure			
		Pholads		Teredos		Pholads		Teredos	
		Surface Penetra- tions	Intensity of Attack (penetra- tions/dm ²)	Surface Penetrations	Etches	Surface Penetrations	Intensity of Attack (penetra- tions/dm ²)	Surface Penetrations	Etches
Control formulation	1	60(47)†	5.89	29(0)	31	39(28)	5.74	12(0)	29
DOP + 1.3% aldrin	I-18	30(23)	5.88	0	—	22(14)	6.47	0	1
DOP + 2.6% aldrin	I-19	28(16)	5.50	0	2	21(12)	6.17	0	—
DOP + 1.3% dieldrin	I-20	25(15)	4.90	0	—	30(23)	8.83	1(0)	—
DOP + 2.6% dieldrin	I-21	20(7)	3.92	0	1	19(14)	11.19‡	0	—
DOP + 1.3% lindane	I-22	26(21)	5.10	1(0)	—	17(15)	5.00	1(0)	1
DOP + 2.6% lindane	I-23	24(19)	4.70	0	—	36(24)	10.60	4(0)	4

* For complete formulations consult Table 1.

† The parenthesized figure is the number of perforations of the plastic.

‡ Only one specimen retrieved.

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Table 4
Effect of Plasticizer Variation on Resistance of Polyvinyl Chloride to Marine Borer Attack

Abbreviated Formulation*	Form- ula No.	8 Months' Exposure					14 Months' Exposure				
		Pholads		Teredos			Pholads		Teredos		
		Surface Penetra- tions	Intensity of Attack (penetra- tions/dm ²)	Surface Penetra- tions	Intensity of Attack (penetra- tions/dm ²)	Etches	Surface Penetrations	Intensity of Attack (penetra- tions/dm ²)	Surface Penetra- tions	Intensity of Attack (penetra- tions/dm ²)	Etches
Control formulation	1	22(10)†	1.67	7(1)	0.53	11	32(22)	3.30	32(1)	2.76	32
50 DOP/50 creosote	23	9(5)	1.77	0	0	14	6(2)	1.76	3(0)	0.88	28
o-Tricresyl phosphate	I-9	10(3)	1.96	1(0)	0.20	11	17(10)	5.00	9(0)	2.65	13
Diocetyl adipate	I-25	6(4)	1.17	5(0)	0.98	3	11(10)	3.24	11(0)	3.24	11

* For complete formulations consult Table 1.

† The parenthesized figure is the number of perforations of the plastic.

Table 5
Interrelation Between Plastic 'Hardness' Achieved by Reduction of Plasticizer and by Addition of Inert Filler on the Resistance of Polyvinyl Chloride to Marine Borer Attack

Abbreviated Formulation*	Form- ula No.	8 Months' Exposure				14 Months' Exposure			
		Pholads		Teredos		Pholads		Teredos	
		Surface Penetrations	Intensity of Attack (penetrations/dm ²)	Surface Penetrations	Intensity of Attack (penetrations/dm ²)	Hardness	Surface Penetrations	Intensity of Attack (penetrations/dm ²)	Surface Penetrations
1/3 Reduction in DOP	3	10(5)†	1.96	2(0)	0.39	22‡	3(2)	0.88	7(0)
1/3 Reduction in DOP + SiC (270-400 mesh)	26	4(0)	0.79	0	—	80	11(1)	2.94	0
SiC (270-400 mesh)	12	5(2)	0.98	0	—	60	4(2)	1.18	0
									20
									15
									0

* For complete formulations consult Table 1.

† The parenthesized figure is the number of perforations of the plastic.

‡ Shore type D durometer; all others shore type A durometer.

Wood Damage

Wood damage was rated to assess the amount of borer activity and to aid in evaluating the relative damage sustained by the plastic specimens. This rating is presented in Table 6 as a function of each wood face and is based on the digital rating system presented earlier. As might be expected, damage to the wood at the wood/plastic interface was most heavy in the completed sandwich; the wood/plastic interface of the section of wood that backed up the lower, exposed portion of the plastic (face c) was much less damaged. The warping and swelling of many of the plastics and the looser contact in general between the plastic and the wood were probably the mitigating circumstances responsible. Except for the harder (and stiffer) plastics, this ill-defined wood/plastic interface was probably regarded by the tunneling animals as a normal wood/water interface which they would not breach. For the harder, more rigid specimens, the damage at this interface was greater. Generally speaking, borer damage sustained by a plastic specimen is partially related to the damage sustained by the wood members of the sandwich. A correlation can be found by comparing the data of Table 6 with that of Table 7 which depicts the average pholad damage for all plastic specimens as a function of panel face, defined earlier. Not only does the damage sustained by the wood and the specimens increase with exposure time, as would be expected, but a relationship also exists in the amount of damage between corresponding wood and plastic faces. Finally, one of the vagaries of nature encountered in rating the plastics was the variability in attack on the wood by the boring organisms. Many of the specimens sustained little damage, not because they were particularly resistant to borer activity, but because the wood was less heavily infested and fewer (or no) organisms reached the plastic surfaces. Such nonuniform response tempers assimilation of the data.

Plastic Damage by Pholads

Virtually all of the damage sustained by the plastic specimens was caused by pholads, and most of this damage by animals that had worked their way through the thinner mahogany member of the sandwich, as shown by the data in Table 7. There were relatively few instances where pholads were found actively boring into the lower half of the plastic opposite the face exposed directly to the water. As mentioned earlier, in many cases this portion of the plastic was prone to swell and warp, thereby rendering the wood surface beneath a quasi-exterior surface through which the organisms would not penetrate. Pholad data have been entered for each of the formulations listed in Table 2. However, all comparisons have been made between groups of formulations having a common function. An intensity of attack has been derived for each of these groups by summing the surface penetrations sustained by each of the formulations within a group and dividing by the total area of the plastic specimens in that group juxtaposed with the wood. The parenthesized figures in all the tables refer to the number of perforations for the formulations in question.

Reduced Plasticizer and Inert Fillers—The intensity of attack (penetrations/dm²) at the end of 14 months for the group of formulations whose hardnesses were increased by a systematic reduction of plasticizer content was not significantly different from the intensity of attack on the control formulations as determined by application of the Student's *t* test, a test for the significant difference between two means. Similarly, no significant difference could be shown between the intensity of attack on the controls and on the group of formulations containing the inert fillers, although, as will be seen later, this latter group of plastics was very resistant to damage by teredos.

Table 6
Average Intensity of Attack* on the Wood Portions of the
Specimen Sandwiches by Face

Location of Specimens	Face	Damage Rating (penetrations/dm ²)			
		6 Months	8 Months	12 Months	14 Months
Naos Island	a	—	1.55	—	2.48
	b	—	1.32	—	2.61
	c	—	0.68	—	0.91
Coco Solo	a	1.88	—	2.73	—
	b	1.42	—	2.75	—
	c	0.50	—	1.25	—

*0 = none, 1 = light, 2 = moderate, 3 = heavy.

Table 7
Average Intensity of Pholad Attack on the Plastic Specimens by Face

Location of Specimens	Face	Damage Rating (penetrations/dm ²)			
		6 Months	8 Months	12 Months	14 Months
Naos Island	a	—	1.43	—	3.93
	b	—	0.84	—	2.92
	c	—	0.34	—	0.36
	d	—	0.0	—	0.0
Coco Solo	a	7.42	—	10.10	—
	b	2.04	—	3.91	—
	c	0.29	—	0.21	—
	d	0.0	—	0.0	—

Non-PVC Polymers—Again by Student's *t* test the NRL-formulated non-PVC polymers were affirmed more resistant to borer damage than the control formulations, although they have the same hardness range as the controls and as the formulations containing the inert fillers. Except for the crosslinked polyethylene, which was a much harder plastic, this resistance is possibly being provided by a physical peculiarity of these plastics akin to a combination of toughness and elasticity. Through microscopic observation of the cutting process (13), it was found that when a cutting edge is brought into contact with the surface of one of these materials it is unable to penetrate this surface unless considerable pressure is applied; instead, the plastic tends to flow around the advancing blade. And in the case of a needle puncture, these materials retain little memory of the event, since only a slight wound—no entrance hole as in the case of the PVC plastic—remains after the needle has been withdrawn. It is plausible that these plastics similarly flow around the denticulations of a pholad's shell as it moves

against the surface of the plastic, thereby requiring greater effort on the part of the animal to abrade that surface.

Other evidence has been gathered which supports the hypothesis that the physical nature of these non-PVC polymers may be a significant factor contributing to their resistance to damage by pholads and teredos. All of the flexible non-PVC polymers have shown more initial resistance to termite attack than PVC plastics of the same hardness (14). To understand why, microscopic observation of a simulated termite pincing mechanism in action was carried out in the laboratory. In such trials these plastics were observed to slip out from between the closing pincers analogously to the advancing knife blade rather than being caught up in a polyp. This action suggests that the termites are unable to gather—or gather with difficulty—polyps of the material between their mandibles. Thus, in both types of exposure the resistance of these formulations can be attributed to a physical property of the plastic. The correlation between the exposure data of these polymers with regard to damage by such diverse organisms as marine borers and termites is worthy of further study.

Plasticizer Effect—The effect of changing the plasticizer from DOP used in the control formulation can be seen from the data in Table 4 and, graphically, in Fig. 4. Those panels containing the DOP/creosote plasticizer mixture were not damaged as much by pholads at the end of the exposed period as those of the control formulation which was plasticized with DOP. Toxicity of the creosote is not a factor in this instance because evidence shows (13) that adult pholads are capable of boring from a wooden bait piece into treated pine containing as high as 37 lb/cu ft of creosote, and to continue boring actively into this heavily treated wood. At the end of 14 months those panels containing o-TCP (30 wt-% in TCP) were considerably more damaged than those of the control formulation.

Specimens containing DOA as the plasticizer were about as susceptible to pholad attack as the controls; however, these specimens behaved uniquely by shrinking very badly and becoming quite hard and brittle. The initial hardness value (Shore A durometer) was 63; after 8 months' exposure it had increased to about 90 (Shore A durometer), while at the end of 14 months the remaining specimens had a hardness of about 60 (Shore D durometer). This formulation, as compounded, contained 39% plasticizer (15); at the termination of exposure, the plasticizer content had decreased to 23% for the plastic within the sandwich and to 8% for the plastic exposed directly to the water. This increase in hardness, which is attributed to the loss in plasticizer, was also observed to occur in jungle exposures of this formulation (11). On the basis of these observations, DOA is not recommended as a plasticizer in the compounding of PVC formulations, particularly where these formulations are to be used in natural environments.

One experimental plastic was prepared which combined increase in hardness achieved by reduction of plasticizer and increase in "internal hardness" achieved by addition of an inert filler SiC (270-400 mesh). The performance of this formulation is compared in Table 5 with that of formulations incorporating only the reduction in plasticizer or the inert filler. Inspection of the data shows that the combination of these variables provided no advantage over those formulations containing these variables separately. In fact, the 14-month pholad data show the combination to be much more susceptible than the control formulations to damage by these animals which typifies the anomalous results frequently encountered in working with natural biological systems.

Toxicants—Those PVC plastics exposed in the extremely borer-active Caribbean waters at Coco Solo constituted a group of formulations containing the toxicants aldrin, dieldrin, and lindane at two different concentrations (Table 1). The results of this exposure,

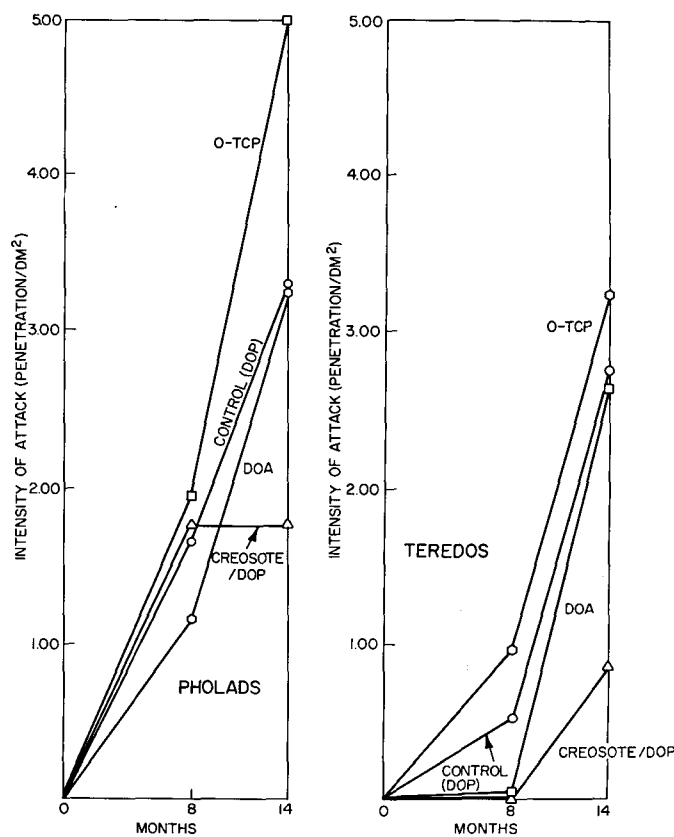


Fig. 4—Relationship between the intensity of attack and exposure time as a function of plasticizer changes made in the basic formulation

presented in Table 3, indicate that none of the toxicants were effective in preventing infestation by pholads. The ineffectiveness of these toxicants, and of the creosote and o-TCP mentioned above, against adult pholads may be related to their methods of boring and feeding. Unlike teredos, pholads receive all their nourishment via their incurrent water siphon. Also, none of the debris resulting from their boring activity passes through the gut where toxic substances could be absorbed. In *Martesia*, as in other pholad species, the majority of this debris is removed from the anterior end of the burrow and ejected as pseudofeces through the incurrent siphon in a backflushing operation performed by the animal (16). Apparently toxic substances incorporated into a substrate have no way of being ingested by pholads so that their control by chemical means may be difficult. However, it has been reported (17) that copper-containing preservatives, particularly those containing copper naphthenate, are effective. In addition to penetrating the plastic specimens, pholads were observed on occasion to partly or completely sever the 1/4-in. nylon-threaded rod used to hold the sandwiches to the mounting spline as shown by the severed rod in Fig. 5.

Plastic Damage by Teredos

In rating the plastic specimens for teredo damage, a tabulation was kept of the number of penetrations of the plastic surface, the number of perforations of the plastic, and the number of etchings on the surface; an etching was defined as a mark or scar left on the plastic

by teredo activity which was not accompanied by a discernible indentation of the surface. The data collected at Naos Island are presented for most of the formulations in Table 2; the remainder are given in Tables 4 and 5. Data collected at Coco Solo are presented in Table 3. Since the etching caused no damage to the plastics, these data have been included in the tables only as an indication of borer activity at the wood/plastic interface.

Very little teredo damage was sustained by any of the formulations fabricated in the laboratory, irrespective of exposure location, and all of this damage took place within the sandwich. Only two teredo etches were recorded on the nonsandwiched half of the plastic for all the specimens combined. In almost every case where a teredo broke through the wood, the animal turned and bored parallel to the plastic surface, depositing the typical calcareous tunnel lining against the specimen. Occasionally, an animal succeeded in making more than a light etch of the surface. When indentations occurred, they were rarely over 1 millimeter in depth and were in the form of gouges into the plastic made as the animal negotiated a turn and proceeded parallel to the plastic. Frequently, the gouge would be elongated into a furrow several millimeters in length before the animal would turn back into the wood. In only two instances were teredos able to perforate PVC formulations and both of these perforations occurred on control specimens. The teredo data have been treated in the same manner as that for pholads. An intensity of attack has been derived for each of the plastic groups in Table 2, and each value is compared to that of the controls.

Reduced Plasticizers—Comparison by Student's *t* test between the formulations having reduced plasticizer and the controls does not refute the null hypothesis that no difference exists between the two sets of data. So if hardness has a beneficial effect, the data do not substantiate it.

Non-PVC Polymers—Statistical treatment of the 14-month exposure data provided by the NRL-formulated non-PVC plastics affirms that this group is more resistant to teredo damage than the controls. Only ten surface penetrations of these plastics were recorded after 14 months, and one formulation, ethylenepropylene rubber, sustained no damage at all. The hypothesis regarding the resistance of these non-PVC polymers proposed earlier is relevant here.

Inert Fillers—The data obtained at 14 months from the group of formulations containing the inert fillers indicate that these materials are very resistant to teredo damage. Although the attack on the mahogany parts of these sandwiches ranged from moderate to heavy, and numerous teredo tunnels had broken through the wood surface and extended parallel to it for several millimeters in many cases, very little teredo activity, including etching, was recorded with respect to these formulations as shown in Table 2. It seems highly improbable that the specimens of this group, randomly distributed within the exposure arrays as they were, would all achieve the same rating by chance. Apparently the presence of these inorganic



Fig. 5—Nylon mounting rod severed by pholad activity

fillers was somehow able to discourage teredos from trying to burrow into these plastics, even to the extent of just etching the surfaces. As will be seen below, the influence of an inorganic filler was also apparent in the formulation which contained both an inert filler and reduced plasticizer in that this formulation behaved more like the formulations of the inert filler group in its resistance to attack. It is interesting to note in connection with these inert fillers that the presence of siliceous inclusions in the ray cells of certain woods has been correlated with the ability of these woods to resist damage by teredine borers (18).

Toxicants—A similar pattern of attack (or lack of attack) to that of the inert filler group was observed for the formulations exposed in the bioactive waters at Coco Solo as presented in Table 3. In this case, however, the formulations were characterized by the addition of the toxic materials aldrin, dieldrin, or lindane, respectively. It can be hypothesized that small amounts of these materials had diffused into the wood surface and served to repel animals as they entered this diffusion zone. Unlike pholads, teredos (19) have no way of eliminating wood debris scraped from the advancing end of the burrow except to pass it through the alimentary tract where much of it is broken down into simpler substances, which constitute the major source of energy for these animals. If this wood became contaminated by diffusion of the toxicants, it is not unreasonable to suggest that this contamination could be sensed by the burrowing animals, causing them to turn away from the wood/plastic interface.

Substitution of TCP or DOA for DOP in the basic formulation did not improve its performance as shown by the data in Table 4 and graphically in Fig. 4. However, the formulation which contained the plasticizer composed of a 50/50 mixture of DOP and creosote performed better than the controls in that there were only three penetrations of the plastic surface at the end of 14 months even though teredo activity was good at the interface as indicated by the number of etchings recorded. Thus, the presence in the plastic of creosote, which has a long history of wood protection against teredos, had a beneficial effect. These specimens still had a strong creosote odor when they were removed from the water after a 12-month exposure. It should be noted, however, that the protective influence of creosote observed in this instance was absent in an earlier exposure (20), which showed little lateral diffusion of toxicant from creosoted-impregnated wood into adjacent untreated wood, thereby offering little protection to the latter.

As mentioned previously, the performance of the formulation which combined reduced plasticizer content with the addition of an inert filler was equal to that of the formulation containing the inert filler (silicon carbide) alone, in that neither formulation sustained any teredo damage as shown in Table 5; the formulation containing one-third reduction in plasticizer bore surface penetrations caused by teredos, as did the other members of the reduced-plasticizer group (Table 2). These results suggest that the adjustment of "internal hardness" by the addition of inert fillers is more beneficial in protecting the plastic from teredo damage than an adjustment in true hardness achieved by plasticizer reduction.

General Comments

In this study, none of the formulations sustained any marine borer damage to the plastic face exposed directly to the water. Instead, this face was always fouled, to varying degrees, by both soft and hard fouling organisms. A typical fouled array from Naos Island is shown in Fig. 2; the fouling at Coco Solo was much heavier and included more barnacles. Occasionally the hard foulers, particularly barnacles, would cut into the plastic surface as the shell increased in size. Also, many of the hard foulers left a pronounced scar on the surface of the plastic when they were removed. The cellulose acetate-butyrate was included in this study as

a proprietary material with a hard surface comparable to that for the PVC formulation containing no plasticizer. The data presented in Table 2 show the extent to which this plastic was damaged by both pholads and teredos. The latter animals succeeded in perforating this material four times and penetrating the surface 40 times; most of these penetrations were much deeper than those occurring in any of the experimental formulations. In this case hardness was no deterrent to the boring activity of these molluscs. The relationship between borer attack and substrate hardness deserves further comment. Table 8 lists all of the harder plastics exposed in this study with their intensities of attack, and DOA, a soft plastic which hardened during the exposure period. Except for certain inconsistencies in the data which reflect nonuniform borer attack, the harder plastics were evidently just as heavily attacked by both teredos and pholads as the softer plastics, represented by the controls. It is suspected that the less-yielding nature of these harder materials facilitates removal of shavings from the surface by the boring organisms and that these shavings are less likely to clog the denticulated ridges of the shell so that rasping action can proceed more efficiently.

Table 8
Damage Rating of the Harder Polymer Formulations Exposed in the
Pacific Ocean (Naos Island)

Abbreviated Formulations*	Formula No.	Hardness†	8 Months Exposure		14 Months' Exposure	
			Pholads	Teredos	Pholads	Teredos
			Intensity of Attack		Intensity of Attack	
Dioctyl adipate (DOA)	I25	63‡	1.17	0.98	3.24	3.24
1/3 Reduction in DOP	3	22	1.96	0.39	0.87	2.06
2/3 Reduction in DOP	4	48	1.96	0.87	4.15	1.38
4/5 Reduction in (DOA)	5	60	1.18	1.37	3.24	2.94
No plasticizer	21	80	0.87	0.65	2.94	0.59
Cross-linked polyethylene	24	55	0.59	0.0	2.65	1.77
Cellulose acetate	CA	76	2.39	4.56	3.53	5.58
Controls	1	53§	1.67	0.53	3.30	3.30

* For complete formulations consult Table 1.

† Hardness of unexposed plastics—Shore type D durometer (Except final DOA and Controls).

‡ Initial hardness was 63 (Shore type A durometer); Final hardness after exposure was 60 (Shore type D durometer).

§ Shore Type A durometer used.

CONCLUSIONS

None of the plastics used in this study will become infected by larvae of teredos or pholads directly from the water. If, however, articles fabricated from any of these materials are placed, or allowed to remain, in intimate contact with any substrate that could serve as host for these borers until they became established, then damage to the plastics could occur. Consequently, great care should be exercised when using such articles that they are not allowed to remain in juxtaposition with susceptible materials for long intervals.

The non-PVC polymers exposed in this study were the most resistant to damage by pholads and teredos; they were also physically unaffected by long immersion in seawater. These polymers all have good electrical characteristics which, combined with their resistance to borer and water damage, make them the best choice, (except for crosslinked polyethylene which does not have the required flexibility) for such applications as electrical cable insulation.

The PVC formulations containing the inert fillers showed good resistance to teredo activity and would probably have a good service life if used in colder waters where pholads are scarce. The PVC formulations containing the toxicants aldrin, dieldrin, and lindane also were not susceptible to teredo damage; however, these chemicals have been implicated in environmental pollution. Preliminary results indicate that PVC resin partially plasticized with creosote may provide a useful teredo-resistant plastic. Further work should be done to determine the effect of varying the creosote content.

Of the plasticizers used in this study, DOA was the most undesirable because of considerable shrinkage and embrittlement that occurred to the formulation containing this material. These physical changes have been observed in jungle exposures, and the increase in hardness that occurs is attributed to loss of plasticizer from the specimens. Consequently, DOA is not recommended as a plasticizer in compounding PVC formulations, particularly when these formulations are to be used in natural environments.

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REFERENCES

1. L. R. Snoke, Bell System Tech. J. 36, 1095 (1957).
2. R. A. Connolly, Mater. Res. Std. (ASTM) 3, 193 (1963).
3. L. R. Snoke, Bell Lab. Record 35, 287 (1957).
4. W. Coscarelli, *Principles and Applications in Aquatic Microbiology*, H. Heukelekian and N. C. Dondero, editors, New York, Wiley, 1964, p. 113-147.
5. A. J. Munitz, Undersea Tech. 7, No. 5, 45 (1966).
6. R. A. Connolly, J. B. De Costa, and H. L. Gaupp, American Chemical Society National Meeting, Sept. 1969, Org. Coat and Plastic Div. 29, No. 2, 128 (1969).
7. J. S. Muraoka, ASTM Spec. Tech. Publ. 445, June 1969, p. 5.
8. J. S. Muraoka, Naval Civil Eng. Lab. Report R-495, Nov. 1966.
9. J. S. Muraoka, Naval Civil Eng. Lab. Report R-525, May 1967.
10. J. S. Muraoka, Ocean Ind. 6, No. 2, 21 (1971).
11. J. D. Bultman, J. M. Leonard, and C. R. Southwell, "Termite Resistance of Polyvinyl Chloride Plastic—Two Years' Exposure in the Tropics, NRL Report 6601, Oct. 1967.

12. F. J. Gay and A. H. Wetherly, Commonwealth Scientific and Industrial Research Org., Division of Entemology, Tech. Paper 5, 1962.
13. Unpublished NRL data.
14. C. R. Southwell and J. D. Bultman, NRL letter report, Ser. 9655, "Investigation of Termite Resistance of Polymeric Materials, 1969.
15. ASTM D 2124-62T Infrared Spectrographic Analysis of Components in Polyvinyl Chloride Compounds, 1962.
16. R. D. Turner, Museum of Comparative Zoology, Harvard University, private communication.
17. M. McCoy-Hill, Dock and Harbor Authority 48, 219 (1967).
18. C. R. Southwell, J. D. Bultman, B. W. Forgeson, and C. W. Hummer, "Biological Deterioration of Wood in Tropical Environments, Part 2—Marine Borer Resistance of Natural Woods over Long Periods of Immersion," NRL Report 7123, Dec. 1970.
19. C. E. Lane, Scientific Monthly 80, 286 (1955).
20. T. R. Sweeney, J. D. Bultman, and A. L. Alexander, "Marine Borer Control, Part 3—Toxin Diffusion Test," NRL Report 4411, Sept. 1954.

